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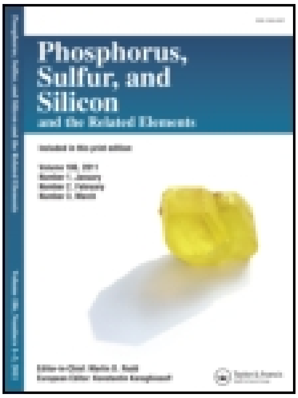

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Microwave-Assisted Esterification of Phosphinic Acids by Alcohols, Phenols, and Alkyl Halogenides

György Keglevich [a] , Nóra Zs. Kiss [a] , Erika Bálint [a] , Erzsébet Jablonkai [a] , Alajos Grün [a] , Mátyás Milen [a] , Dávid Frigyes [b] & István Greiner [c]

[a] Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, Budapest, Hungary

[b] Laboratory of Physical Organometallic Chemistry, Institute of Chemistry, Eötvös University, Budapest, Hungary

[c] Richter Plc, Budapest, Hungary

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MICROWAVE-ASSISTED ESTERIFICATION OF PHOSPHINIC ACIDS BY ALCOHOLS, PHENOLS, AND ALKYL HALOGENIDES

György Keglevich,[1] Nóra Zs. Kiss,[1] Erika Bálint,[1] Erzsébet Jablonkai,[1] Alajos Grün,[1] Mátyás Milen,[1] Dávid Frigyes,[2] and István Greiner[3]
[1]*Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, Budapest, Hungary*
[2]*Laboratory of Physical Organometallic Chemistry, Institute of Chemistry, Eötvös University, Budapest, Hungary*
[3]*Richter Plc, Budapest, Hungary*

Abstract *Cyclic phosphinic acids undergo direct esterification with alcohols at ca. 200°C under microwave conditions.*

Keywords Esterification; green chemistry; microwave; phase transfer catalysis; P-heterocycles; phosphinic acid

Phosphinic acids do not undergo direct esterification; for this, phosphinates are usually prepared by the reaction of phosphinic chlorides with alcohols. We have found that phenylphosphinic acid could be esterified with butanol under microwave (MW) irradiation at 180°C to give PhP(O)H(OBu) in 90% yield.[1] The MW-assisted direct esterification could be extended to 1-hydroxy-3-phospholene 1-oxides (**1**), 1-hydroxy-phospholane 1-oxides (**3**), and a 1-hydroxy-1,2,3,4,5,6-hexahydrophosphinine 1-oxide (**5**) to afford cyclic phosphinates **2**, **4**, and **6**, respectively. Using an excess of butanol or propanol at 180–230°C, the best yields amounted to ca. 60% (Scheme 1).

The cyclic phosphinates (**2**,[2] **4**, and **6**) could also be prepared by alkylating esterification of the cyclic phosphinic acids (**1**,[2] **3**, and **5**) under MW conditions at 100–120°C. It was found that using alkyl halogenides of normal reactivity (e.g., EtI, PrBr, and BuBr), the presence of triethylbenzylammonium chloride (TEBAC) as the phase transfer catalyst was synergetic with the MW irradiation. At the same time, applying benzyl chloride, that is, of increased reactivity, MW irradiation was beneficial without the use of TEBAC (Scheme 1).

It was found that 1-hydroxy-3-phospholene oxides **1** were more reactive than the phospholane- and the hexahydrophosphinine derivatives (**3** and **5**, respectively). The reason for this may be because in the case of a fully saturated ring moiety, both the nucleophilicity of the P=O group and the acidity of the P(O)OH function are decreased.

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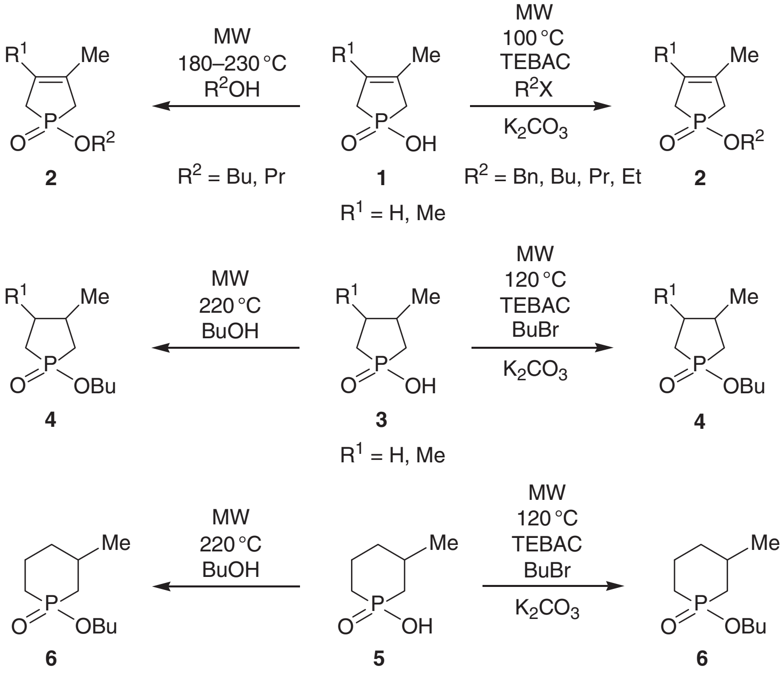
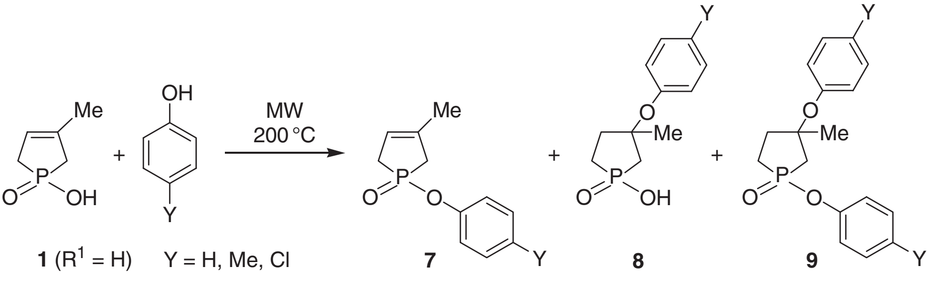
Address correspondence to György Keglevich, Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, Budapest, Hungary. E-mail: gkeglevich@mail.bme.hu



Scheme 1

Using phenol derivatives as the reactant in MW-assisted esterification of hydroxy-phospholene oxide **1** ($R^1 = Me$), the desired ester (**7**) was formed only in a small quantity ($\leq 3\%$); adduct **8** and adduct-ester **9** were also present in the reaction mixture (Scheme 2).



Scheme 2

Further studies to explore the possibilities offered by the above reactions are in progress.

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